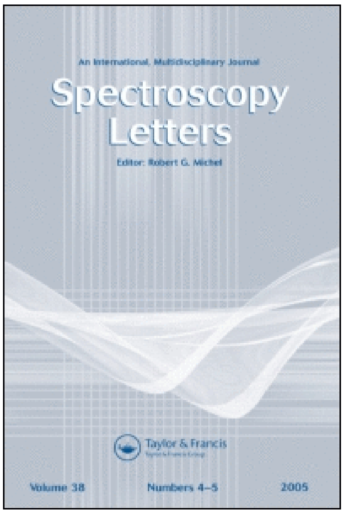

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Yang, Karl X. , Swami, Kamal and Husain, Liaquat(2009) 'Sensitive Measurement of Se and Te in Cloud Water and Ambient Particulate Matter', Spectroscopy Letters, 42: 8, 458 — 466
To link to this Article: DOI: 10.1080/00387010903267179
URL: http://dx.doi.org/10.1080/00387010903267179

Spectroscopy Letters, 42:458–466, 2009
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ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010903267179

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Sensitive Measurement of Se and Te in Cloud Water and Ambient Particulate Matter

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ABSTRACT Analytical methods have been developed to measure low levels of trace elements (Te and Se) in cloud droplets and aerosol particulates. For water collected from cloud droplets, pneumatic nebulization coupled with inductively coupled plasma mass spectrometry yielded sufficient sensitivity to allow measurement of Se and Te after a 20-fold hotplate preconcentration. In cloud water samples collected on July 23, 1995, at Whiteface Mountain, New York, USA, Se and Te concentrations appeared to track one another, suggesting that Te could become a viable tracer element given that Se is already a proven tracer in the study of oxidation of SO_2 into SO_4^{2-}. For aerosol filter samples, a microwave digestion scheme was developed to dissolve the sample, resulting in highly diluted Se and Te concentrations, too low to be measured by pneumatic nebulization inductively coupled plasma mass spectrometry Hydride generation inductively coupled plasma mass spectrometry was used to improve the detection limits of Se and Te by a factor of 30. It enabled the detection of Se and Te in the low ng/L range in aqueous solution, or in the pg/m^3 range in aerosol samples. An aerosol particulate standard (SRM1648, Urban Particulate Matter; NIST) and a sediment standard (GSD11; Institute of Geophysical and Geochemical Prospecting of China) were digested and analyzed to validate the methods.

KEYWORDS aerosol, cloud water, ICPMS, selenium, tellurium, trace measurement

INTRODUCTION

Human activities, such as fossil fuel combustion and various industrial processes, introduce large amounts of sulfur and nitrogen oxides into the atmosphere. The oxides can be deposited directly to surfaces and converted to sulfuric and nitric acids via aqueous oxidation processes in cloud and fog droplets. Alternatively, the oxides can undergo homogeneous oxidation to their respective acid and subsequently deposited to surfaces through wet (rain and snow) and dry processes. There is a growing body of evidence that indicates that acid aerosols and precipitation negatively affect both human health and the environment.[1,2] Many pollutants remain in the atmosphere

Received 12 January 2007;
accepted 9 August 2007.

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for several days, during which time they may be transported great distances from their emission source.[1,3] During the transport, some pollutants can undergo complex reactions in both the homogeneous and heterogeneous phases. Various tracer techniques have been developed to study the transportation and transformation of pollutants in the atmosphere.[4] Husain[5] developed a technique based on the SO_4^{2-} /Se ratio to determine in-cloud formation of SO_4^{2-} from the oxidation of SO_2. In a subsequent paper from that group, arsenic and antimony were included in the tracer list.[6] In this technique, the in-cloud formation of was calculated by measuring the concentrations of SO_4^{2-} and Se in both cloud water and ambient aerosols, with the assumption—based on the similarities in their physical and chemical properties—that SO_4^{2-} and Se undergo similar aerosol transportation processes. The equation for calculating in-cloud formation of SO_4^{2-} can be written as:

$$\left(SO_4^{2-}\right)_{in} = \left[\left(\frac{SO_4^{2-}}{Se}\right)_{cw} - \left(\frac{SO_4^{2-}}{Se}\right)_{aa}\right] \bullet (Se)_{cw},$$

where $\left(SO_4^{2-}\right)_{in}$ is the concentration of sulfate formed in-cloud, $(Se)_{cw}$ is the Se concentration in cloud water, and $\left(SO_4^{2-}/Se\right)_{cw}$ and $\left(SO_4^{2-}/Se\right)_{aa}$ are the concentration ratios between sulfate and Se in cloud water and in aerosol, respectively. The success of this tracer technique depends on the accurate determination of the trace element (usually in the low ng/L level in cloud water or pg/m^3 level in air) in both cloud and aerosol samples.

Among many trace metal analysis techniques, inductively coupled plasma mass spectrometry (ICPMS) is the most widely used, due to its multielement capability and sub-ppt (ng/L) detection limits for many elements.[7] Cloud water samples are usually introduced by pneumatic nebulization (PN), either directly or after simple preconcentration by hotplate, into the ICPMS system for analysis.

The analysis of aerosol samples is more problematic, since sample dissolution is usually required prior to analysis. Aerosol sample dissolution can best be carried out by microwave digestion.[8] Concentrated nitric acid (HNO_3) is generally the first choice, because it strongly oxidizes organic matter (such as Whatman cellulose filter paper in this application) and, hence, breaks down the complex hydrocarbons into water and carbon dioxide. Nitric acid forms water-soluble salts with most elements; thus, there is no loss due to precipitation. Nitric acid also introduces minimal matrix effect to the ICPMS system because H, N, and O are common components in the plasma.

Tellurium is potentially a better tracer element than Se for the study of SO_2 and SO_4^{2-} transportation and transformation in the atmosphere, since it is chemically less active while placed in the same group on the periodic table as sulfur and Se. In the earth's crust, the average abundance ratio between Se and Te is estimated to be between 15 and 45.[9] Tellurium is less widely used in industry than is Se; hence, samples are less likely contaminated by local sources. However, accurate determination of Te in environmental samples remains a challenge. Tellurium is an extremely rare element in the earth's crust,[10] where its concentration can be below 1 ng/g. In a typical digestion scheme, where 2 mg of sample is digested and diluted to 25 mL, the concentration of Te would be 0.08 ng/L, far below the detection limit achievable by ICPMS.[11] Nevertheless, Te levels in aerosols are usually found to be higher due to the enrichment by industrial processes.[12]

Hydride generation (HG) is an effective sample introduction method for improving the detection limits of Se and Te measured by ICPMS.[13,14] It converts the analyte dissolved in the aqueous phase into the gas phase, which is subsequently swept into the inductively coupled plasma (ICP) torch for analysis. The potential interfering concomitants are left behind in the solution, and thus, low detection limits are usually achieved due to minimized matrix interference. The drawback is that samples need to be treated with 50% HCl to reduce Te^{6+} to Te^{4+}, which is a preferable valence state for HG. Such sample pretreatment is time consuming and potentially prone to chemical interference.

In this article, the use of ICPMS for measuring trace amounts of Te in cloud water and aerosol particulates is investigated. Se was also measured for reference and comparison purposes, since its chemical characteristics are better known, and since it, like Te, can readily be converted into its hydride form. PN and HG were studied as sample introduction methods for cloud water and aerosol particulate samples. Potential matrix interference was investigated. Independent quality controls (QCs) and standard reference materials were used to validate the methods. The potential of using Te as a tracer in studying the oxidation of SO_2 in the atmosphere is evaluated.

EXPERIMENTAL

PN-ICPMS

An HP4500 ICPMS (Agilent Technologies, Wilmington, Delaware, USA), equipped with Chem-Station Software and a Cetac Technologies ASX 500 autosampler (Cetac Technologies, Omaha, Nebraska, USA), was used for the experiment.

HG-ICPMS

An integrated sample introduction HG system (ISIHGS) (Agilent Technologies, Wilmington, Delaware, USA) was coupled to the ICPMS for these experiments. The detailed description of the system and the advantage of using a non-robust plasma for HG-ICPMS has been published elsewhere.[15]

For daily operation, a tuning solution consisting of 2 μg/L of Se and 0.2 μg/L of Te in 50% (v/v) HCl was used for optimizing the system. These concentrations were chosen to represent the typical values in samples. Tellurium hydride was found to have a severe memory effect; calibration or QC solutions were prepared to be <2 μg/L for Te to avoid extending rinsing time. The calibration concentrations were 0, 0.1, 0.2, 0.5, and 1 μg/L for Se, and 0, 0.01, 0.02, 0.05, and 0.1 μg/L for Te. QC solutions from an independent source were used. The typical conditions for achieving interference-free analysis were: RF power, 785 W (warm plasma); Ar carrier gas, 0.44 L/min; and Ar blend gas, 0.87 L/min.

Isotopes of ^{80}Se, ^{82}Se, ^{125}Te, and ^{130}Te were monitored. The conditions and sensitivities of the instrument varied daily, but the ^{82}Se/^{80}Se ratio was tuned to be between 16% and 17%, while the signals on the masses of 82, 125, and 130 were maximized. Both the samples and the calibration solutions were prepared in a 50% (v/v) HCl medium and were incubated in a 80°C water bath for 20 min to ensure the complete conversion to valence 4 state for Se and Te prior to HG.[16] The reducing reagent containing 0.2% (w/w) $NaBH_4$ and 0.05% (w/w) NaOH was freshly prepared daily.

Microwave Digestion of the Standard Reference Material

The methodology for analyzing aerosol samples was developed based on the recoveries of Se and Te on two standard reference materials made from real world solid samples: Urban particulate matter (SRM1648; NIST, Gaithersburg, Maryland, USA) and a stream sediment reference material (GSD11) from the Institute of Geophysical and Geochemical Prospecting of China (IGGPC).

The standard reference materials were digested by the use of a microwave oven (model CEM MARS 5; CEM Corporation, Matthews, North Carolina, USA) to dissolve the analytes into aqueous solution prior to analysis. The microwave oven and the detailed digestion methodology have been described elsewhere.[17,18] Prior to use, the Teflon vessels were first soaked in detergent solution and ultrasonicated for 30 min and then soaked in 35% (v/v) HNO_3 overnight. After being rinsed thoroughly with deionized distilled water (DDW), the vessels were filled with 10 mL of 0.1-M nitric acid and heated in the microwave oven under the same conditions as were used for the sample digestion. After being cooled, they were flushed once more with DDW.

Two mL of concentrated HNO_3 and 4 mL H_2O_2 were added, with 2 mg of SRM1648 or 50 mg of GSD11, in a vessel. The vessels were capped, placed in the microwave system, and digested using the following procedure.

The temperature was ramped to 170°C within 15 min with the application of 1200 W of power followed by a dwell time of 2.5 min, and then heating to 185°C within 3.0 min at 1200 W followed by a dwell time of 10 min. The vessels were then removed from the oven and cooled in a freezer at −20°C for 1 h; they were then vented and opened. The samples were transferred to graduated polypropylene centrifuge tubes and diluted with DDW to a final volume of 25 mL. Along with each batch, a reagent blank and two filter paper blanks were prepared and carried through using the same procedure as the samples.

Hotplate Preconcentration

No digestion was needed for cloud water samples, since Se and Te are readily soluble in water. However, the two elements' concentrations (especially that of Te) were near or below the detection limits for PN-ICPMS. A 20-fold preconcentration of each sample was done by evaporating the solvent in a 68°C water bath to increase the analyte concentrations sufficiently above the detection limits.

The temperature was kept at 68°C to prevent the escape of volatile Se or Te chemical species from the solution. The original cloud samples had been acidified so as to contain 0.15% (v/v) of HNO_3 in order to preserve the metals. After preconcentration, the concentration of HNO_3 was increased by 20 fold, to 3% (v/v). However, the preconcentration method is not suitable for the aerosol particulate solution after microwave digestion, since, in this case, the HNO_3 concentration is initially much higher; preconcentration would have increased the acid level to the extent of inducing severe matrix effects. Other preconcentration methods such as solid-phase extraction and liquid-liquid extraction have proven to be rapid and efficient,[19,20] but no method was available in the literature for simultaneous extraction of Se and Te with equal efficiency.

RESULTS AND DISCUSSION

Matrix Interference in PN-ICPMS

Matrix effects can be categorized into two types: spectral interference and nonspectral interference. Spectral interference includes isobaric interference (caused by elements having the same m/z value) and polyatomic interference (caused by matrix-induced molecular species such as oxides, argides, nitrides, and dimers). Nonspectral interference refers to the matrix-induced signal intensity changes, regardless of the presence of spectral components; it is due to the matrix-induced factors, which exert an influence on sample transportation, ionization in the plasma, ion extraction, or ion throughput in the resultant ion beam.

The matrix interference on Se has been studied elsewhere,[21] so only Te will be discussed here. Since there are no known isobaric spectral interferences for ^{125}Te, polyatomic interference is the major concern for the detection of ^{125}Te. The polyatomic species that can contribute to the counts at $m/z = 125$ include PdO, AgO, NiNi, SnH, RbAr, and YAr. Single-element solutions of Pd, Ag, Ni, Sn, Rb, and Y were prepared, and each solution was tested for ion counts at $m/z = 125$. Each 10 mg/L Pd, Ni, and Y single-element solution induced ion counts equivalent to that from a blank calibration solution; therefore, no further investigation of these three elements in terms of spectral interference was needed. It was especially encouraging to see that there is little interference from Y, since it is a commonly used internal standard. Any sizable interference caused by Y would have forced us to seek an alternative, and possibly less effective, internal standard.

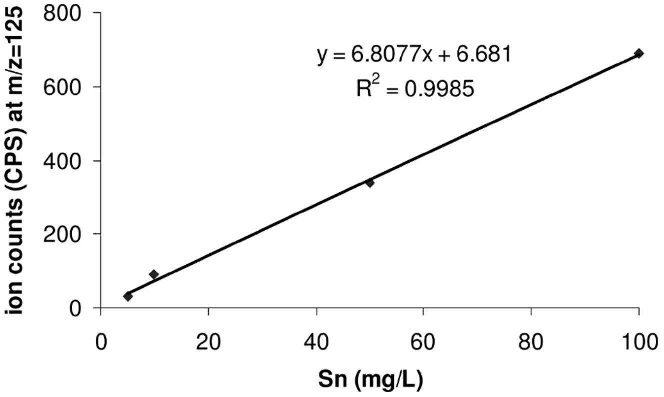

FIGURE 1 Ion counts per second (CPS) at $m/z = 125$ were measured as a function of Sn concentration (mg/L) to assess potential spectral interference with ^{125}Te caused by SnH.

The contribution from Sn to $m/z = 125$ is illustrated in Fig. 1. The ion counts increased linearly as the Sn concentration increased to 100 mg/L. The R-squared value was 0.9982, and the slope was 6.9. Linearity was not retained when the concentration was increased beyond 100 mg/L. This is probably due to the substantial change of the plasma condition with the introduction of a high concentration of Sn. The equivalent Sn concentration for generating one ion count was 140 µg/L, which is orders of magnitude higher than the Sn concentration in a typical atmospheric sample. Therefore, the potential spectral interference from Sn can be ignored.

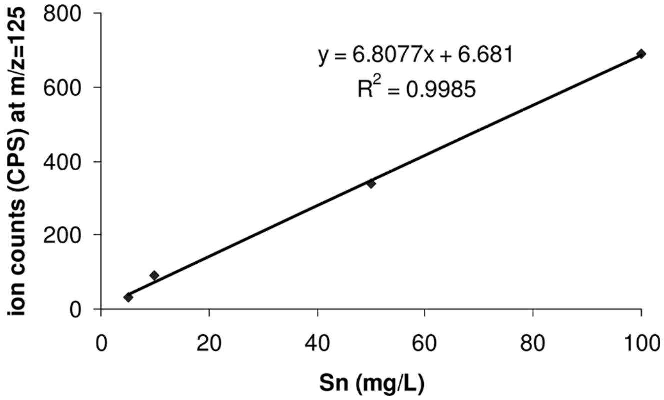

FIGURE 2 Ion counts (CPS) at $m/z = 125$ were measured as a function of Rb concentration (mg/L) to assess potential spectral interference with ^{125}Te caused by RbAr.

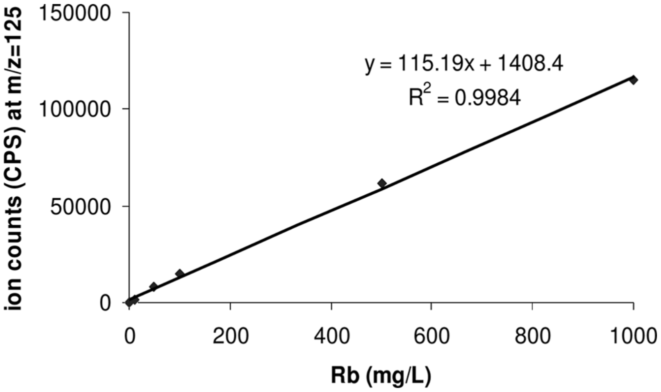

FIGURE 3 Ion counts (CPS) at m/z = 125 were measured as a function of Y concentration (mg/L) to assess potential spectral interference with ^{125}Te caused by YAr.

The contribution from Rb to m/z = 125 is illustrated in Fig. 2. A linear relationship between ion counts and Rb concentration for up to 1000 mg/L was seen. The R-squared value and the slope were 0.9975 and 117, respectively. The equivalent Rb concentration for generating one ion count was 10 µg/L. This concentration is about three times higher than that in a typical digested SRM1648 urban particulate matter sample solution (2 mg sample dissolved in 25 mL solution). Therefore, interference from Rb can also be ignored.

The contribution from Ag to m/z = 125 was studied in a similar manner (Fig. 3). Again, a linear relationship was found when the Ag concentration was lower than 100 mg/L. The R-squared value and the slope were 0.9997 and 16.6, respectively. From the slope, the Ag concentration for generating one ion count was estimated to be 60 µg/L. As is the case for Sn and Rb, this level of Ag is extremely rare in atmospheric samples. Therefore, the potential interference from Ag can be ignored. Similarly to Sn, nonlinearity was observed when the concentration of Ag was higher than 100 mg/L.

Determination of Te and Se in Cloud Water Samples by PN-ICPMS

The detection limit is defined as three times the standard deviation of 12 blank measurements. The detection limits of Se and Te were determined to be 100 ng/L and 30 ng/L, respectively, via PN.

Whiteface Mountain (1.5 km above mean sea level) is located at a rural site in the Adirondack Mountains of New York state in the United States (44° 23′ 26″ N, 73° 5′ 35″ W). Cloud water samples were collected on July 23, 1995 at Whiteface Mountain, starting at 6:00 am and ending at 6:00 pm, EDT. The sampling technique has been discussed elsewhere.[6] Cloud water samples were collected continuously, every 15 min at the summit with a passive collector. The cloud water sampling was discontinued during periods of precipitation. The sample volume varied from 0 to 80 mL, depending on the water content in the cloud and the wind speed at the time of collection. Aerosol samples were also collected on Whatman 41 filters (Maidstone, Kent, UK) using high-volume samplers, but no analysis for Se or Te could be done in this study since the material had been exhausted through analysis and digestion during previous studies. Cloud water samples were acidified with 0.15% nitric acid and stored in a 4°C cooler before analysis. A concentric micronebulizer that consumed about 0.5 mL of solution per run was used; two runs were done for each sample. An attempt was made to measure Te and Se in the original samples, but the concentrations were too low for accurate determination. Slow hotplate evaporation was then applied to preconcentrate the analytes by a factor of 20. The final nitric acid concentration was 3%, within the normal acidity range for ICPMS analysis. Independent QC solutions were used to monitor the preconcentration and calibration accuracy; the measured values were within ±5% of the target values. Table 1 lists the concentrations of Se and Te in the 20-fold preconcentrated cloud samples. Some samples had been exhausted for other research purposes in the past years; therefore, time gaps are present in Table 1. Based on two runs, the relative standard deviation of the Se concentrations of each sample was below 2.2%, indicating stable measurements from ICPMS. The average concentration of Se in 15 cloud samples was 102.8 µg/L, with an RSD of 25.9%; the high relative standard deviation (RSD) was apparently caused by the concentration variation among samples. Also based on two runs, the RSD of the Te concentrations was below 5%. This demonstrates that, with the Te concentration in the original samples in the low ng/L level, precise measurements of Te after 20-fold hotplate preconcentration can be made with PN sample introduction methods. The concentration of Te varied from 0.21 µg/L to 0.58 µg/L, the average was 0.43 µg/L with an RSD of 24.5%; such a high RSD

TABLE 1 **Concentrations of Selenium and Tellurium in 20-Fold Preconcentrated Cloud Water Samples Collected on July 23, 1995, at Whiteface Mountaint, New York, Measured by PN-ICPMS**

Sampling time		Se		Te		
Beginning	End	μg/L	RSD	μg/L	RSD	Se/Te
9:30	9:45	88.7	1.2%	0.39	3.6%	227.3
9:45	10:00	89.1	2.2%	0.39	2.9%	227.3
10:15	10:30	138.0	1.0%	0.58	4.9%	237.9
10:30	10:45	135.0	1.3%	0.54	1.3%	252.2
10:45	11:00	125.8	0.9%	0.49	1.1%	255.7
11:30	11:45	118.0	1.2%	0.50	2.4%	237.7
12:30	12:45	120.9	2.2%	0.50	2.0%	241.2
12:45	13:00	126.7	1.9%	0.52	1.4%	246.0
13:30	13:45	89.4	1.1%	0.37	1.1%	239.5
14:15	14:30	106.7	2.2%	0.48	1.8%	224.1
14:30	14:45	108.2	1.5%	0.44	0.0%	245.8
14:45	15:00	107.1	11.5%	0.44	0.0%	243.4
15:30	15:45	50.0	0.1%	0.25	2.9%	203.9
16:30	16:45	84.8	1.3%	0.33	2.2%	260.9
17:00	17:15	55.1	0.8%	0.21	2.3%	258.1
		ave. = 102.8		ave. = 0.43		ave. = 240.1
		RSD = 25.9%		RSD = 24.5%		RSD = 6.2%

is mainly caused by the concentration variation among samples. The selenium to tellurium ratio was calculated for each sample. The average Se/Te ratio was 240.1, with an RSD of 6.2%; the latter is much lower than the RSDs of individual Se and Te concentrations. This is most likely due to the fact that Se and Te have similar physical and chemical properties, and they tend to have similar fates in the environment. Based on the literature search here, however, this is the first time that Se and Te have been demonstrated to track one another in actual atmospheric environmental samples.

Selenium has been successfully used as a tracer element for the study of SO_2 and SO_4^{2-} transportation and transformation in the atmosphere.[5] Tellurium has the potential to be a better tracer, because it has much fewer natural and anthropogenic emission sources than does Se; thus, Te should be less subject to interference from local sources in the study of long-distance pollutant transportation. Tellurium is more chemically inert than Se; therefore, loss due to chemical transformation is expected to be less. Note that the Se/Te ratio in the cloud water sample was about 5 to 16 times higher than that in the earth's crust, indicating a fairly uniform enrichment factor in favor of Se over Te during the processes that led to the eventual formation of cloud water. However, the quantitative measurement of trace element Te in cloud water and aerosols is significantly more challenging than for Se.

Measurement of Se and Te in the SRM1648 (Urban Particulate Matter) by HG-ICPMS

A preliminary analysis of the microwave-digested reference material (SRM1648) for Te showed that the amount of Te in the sample was too low to be quantified by PN-ICPMS. With 8% (v/v) of HNO_3 already in the sample solution, hotplate preconcentration would have increased the acid concentration to the level that severe matrix interference would have occurred. HG-ICPMS was therefore used for the measurement of Te (along with Se) in this particulate matter.

Detection limits of Te and Se were determined using the optimized conditions described elsewhere.[15] A calibration curve was constructed, and 12 blanks were measured; three times the standard deviation of the blanks was defined as the detection limit. The isotopes ^{78}Se and ^{82}Se yielded detection limits of 3 and 10 ng/L, respectively.

The somewhat poorer detection limit seen for ^{82}Se was probably due to interference from ^{82}Kr, which was introduced into the plasma as an impurity in the argon gas. The detection limit of Te was calculated to be 1 ng/L, same for all isotopes (125, 126, 128, and 130). The detection limits of Se and Te were thus improved by a factor of 30 compared with PN. In the aerosol sampling setup used for this experiment, the air was pulled through the filter at the rate of up to 1 m^3/min for 15 min; the filter was then digested in the microwave oven and diluted to the final volume of 25 mL. Using 1 and 3 ng/L for the detection limits of Te and Se in the solution, we determined the equivalent detection limits of Te and Se in the air sample to be 2 and 6 pg/m^3, respectively.

Table 2 shows the concentrations of Se and Te measured in the SRM1648 digestate without preconcentration. The average recovery of Se from seven samples was 104% with an RSD of 10%. The results illustrate that Se can be completely converted into solution by microwave digestion with nitric acid only, and then accurately determined by HG-ICPMS. The RSD of 10% accounted for accumulated uncertainties during sample preparation and analysis, including sample heterogeneity, and errors from digestion, transfer, dilution, calibration, and data acquisition. Given the number of steps involved and the low amounts of mass (2 mg) and liquid volume (25 mL) being handled, an RSD of 10% is considered satisfactory. Even though 100 mg of SRM 1648 was recommended by NIST for digestion, 2 mg was used since it is closer to the actual amount of aerosol collected on the filter. The mass match-up here was intended to minimize the disparity that the SRM and actual aerosol samples could experience during digestion and analysis, therefore ensuring the validity of the method.

The Te concentration was determined to be 0.99 ± 0.13 μg/g. The accuracy of the determination could not be confirmed due to the lack of a certified value. Nevertheless, for each sample, all four isotopes of Te yielded identical results, strongly indicating that the measurements were interference-free.

Measurements of Se and Te in a Stream Sediment by HG-ICPMS

A stream sediment standard reference material (GSD11) provided by the IGGPC was analyzed for Te and Se. This is one of the very few environmental standard reference materials available that has certified Te and Se values. It has been tested by the Chinese Institute and other institutes around the world and has been found to be exceptionally well prepared and homogeneous.[22] The sample was digested and analyzed using the same procedure as for SRM1648. The measured values and the certified values are listed in Table 3 along with results obtained by other researchers. The measured Se and Te values agree with the certified values within statistical errors. Hall and Pelchat[22] investigated two digestion schemes with hotplate heating: aqua regia and HF-$HClO_4$-HNO_3-HCl. The solutions were analyzed by HG-ICPMS. For Se, the two methods yielded results that were in agreement with the certified value and with the value in this study. For Te, however, only the aqua regia digestion yielded results identical to the certified value and this study's value; the HF-$HClO_4$-HNO_3-HCl digestion in contrast, yielded a 30% positive bias. Nevertheless, this latter value agreed with the measurement made by Kontas and coworkers,[23] who determined Te by graphite furnace atomic absorption spectrometry (AAS) following decomposition with Br_2-HBr and separation by reductive co-precipitation. These differences could indicate that a portion of Te is bound

TABLE 2 **Concentrations of Selenium and Tellurium in Seven Trials of SRM 1648 Measured by HG-ICPMS**

Sample type	SRM 1648, urban particulate matter								
Sample no.	1	2	3	4	5	6	7	Mean	SD
Mass (mg)	2.145	2.65	1.942	1.73	1.836	1.736	2.633	N/A	N/A
Se (μg/L), measured	1.45	1.54	1.09	0.92	0.98	0.98	1.46	N/A	N/A
Se (μg/g), measured	33.80	29.06	28.06	23.83	26.69	28.23	27.73	28.20	2.99
Se (μg/g), certified					27				
Se recovery (%)	125%	108%	104%	88%	99%	105%	103%	1.04	11%
Te (μg/L)	0.050	0.052	0.036	0.031	0.034	0.033	0.061	N/A	N/A
Te (μg/g)	1.17	0.98	0.93	0.980	0.93	0.95	1.16	0.99	0.13

TABLE 3 **Concentrations and Standard Deviation (μg/g) of Selenium and Tellurium from a Stream Sediment Standard Determined in This Work by HG-ICPMS Compared to the Certified Values and Previous Measurement by Hall and Pelchat[22] and Kontas et al.[23]**

			Measured value by other researchers		
			Hall and Pelchat[22]		Kontas et al.[23]
Element	Certified value	Measured value in this work	$HF\text{-}HClO_4\text{-}HNO_3\text{-}HCl$ digestion HG-ICPMS analysis	Aqua regia digestion HG-ICPMS analysis	Br_2-HBr digestion GFAAS analysis
Se	0.20 ± 0.06	0.21 ± 0.03 (4)	0.18 ± 0.1 (3)	0.18 ± 0.1 (3)	N/A
Te	0.36	0.35 ± 0.08 (4)	0.45 ± 0.02 (3)	0.33 ± 0.3 (3)	0.46 ± 0.01 (3)

The numbers of repeats are in parentheses.

as or encapsulated in a silicate matrix. In ambient aerosol particulates, there is much less silicate than in geological samples (such as sediment); it is also likely that Te particulate is physically separated from silicate particulate in aerosol samples, since they originate from two different sources: silicate is from the crust while Te is from anthropogenic sources. Therefore, silicate-bound Te is much less of a concern in ambient aerosol particulates. The full recovery of Se in SRM1648 proved that Se in aerosol particulate can be accurately measured by the use of current digestion and analysis methods. It is highly likely that Te can also be determined with high accuracy. The HG-ICPMS methodology was originally developed for ultra-trace measurement of Se and Te in aerosol particulate; it can also be used for cloud water samples with equal sensitivity. In fact, the same cloud water samples was analyzed with HG-ICPMS, this time, without hotplate preconcentration. The two sets of results agreed with one another within statistical uncertainties.

CONCLUSIONS

PN and HG sample introduction methods were investigated for the accurate determination of Se and Te in environmental samples by ICPMS. Pd, Ni, Sn, Ag, Pb, and Y were studied for their potential interference to Te; no measurable interference is expected for typical environmental samples. PN is suitable for sample introduction of cloud water samples, which have a clean matrix even after 20-fold preconcentration by a hotplate. The Se and Te concentrations in cloud samples appeared to track one another, strongly suggesting that these two elements experience similar fates in the atmosphere after release into the environment. Based on these results, it is, therefore, proposed that Te, like Se, can be used as a tracer element to study chemical transport and transformation in the atmosphere. However, quantitative measurement of trace elements Se and Te in environmental samples is quite challenging. HG is suitable for sample introduction of microwave-digested aerosol samples, which usually contain lower amounts of Se and Te and greater matrix content. The detection limits of both Se and Te were improved by a factor of 30 compared to that for the PN method. An atmospheric aerosol standard (SRM1648; Urban Particulate Matter, NIST) and a sediment standard (GSD11, IGGPC) were digested and analyzed for Se and Te. It appears that some uncertainties still exist regarding the quantification of trace element Te from standard reference materials. However, the Se and Te concentrations determined in this work were in excellent agreement with the certified values, lending much confidence to these analysis techniques.

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